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Crystallization kinetics of polypropylene
Part 4: Effect of unmodified and azide-modified PET and PA short fibres

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Abstract

The effect of short polyethylene terephthalate (PET) and nylon 66 (PA) fibres, and their chemical treatment with an azide derivative, on the PP crystallization kinetics and thermodynamics has been investigated. Both fibres are effective nucleant agents for polypropylene (PP) crystallization, giving rise to the phenomenon of PP transcrystallinity on their surface. However, the presence of azide groups on the chemical structure of the fibres produces a different effect on the PP crystallization kinetics. Azide-modified PET fibres give rise to an additional increase of the global rate of the PP crystallization process, but in this case the transcrystalline development of the PP is not so sensible as in the presence of the unmodified fibres. An opposite behaviour is observed with the azide-modified PA fibres. In general, it can be established for the studied composites that the spherulitic development of the polymer matrix comes from an instantaneous and athermal nucleation whose growth is not constant. It is also suggested that transcrystallinity and a good adhesion at the interface may take place independently one of each other. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Crystallization kinetics; Polypropylene; Polyethylene terephthalate

1. Introduction

The main advantage of thermoplastic composites is the possibility of combining the toughness of thermoplastic polymers with the stiffness and strength of reinforcing fibres, and their ultimate properties depend on the characteristics of the matrix and fibres, as well as on the adhesion strength at the interface.

The microstructure of crystallizable polymers plays an important role on the composite behaviour. The solidification of crystallizable polymers from the melt takes place through the nucleation and spherulite development, and when the solidification process is completed, the total volume of the material is completely full of spherulites. The spherulitic limits are microstructural discontinuities which can modify the behaviour of the material. So, the comprehension of the crystallization kinetics is very important and useful to predict the molding conditions of the material and to correlate the microstructure of the matrix with the processing kinetics.

The influence of fibres on the matrix microstructure arises from their nucleating action. When the nucleating effect is very strong on the fibre surface, the spherulite growth is restricted to the normal direction of the fibre surface, giving rise to the phenomenon known as transcrystallinity. Although transcrystallinity has been reported to improve the mechanical properties of some fibre-reinforced composites [1,2], the mechanism of transcrystallization has not been fully understood and there is no rule to predict the appearance of transcrystallization in a fibre/matrix system. Many factors, such as fibre topography, surface coating of the fibre, and processing conditions of the composites, have been reported to influence the nucleation of transcrystallization to some extent [3–5].

Some fibres, such as carbon and aramide fibres, give rise to polypropylene (PP) transcrystallization [6,7]. However, glass fibres do not cause that phenomenon [8] although it has been demonstrated that in some cases, when the fibres are covered with specific nucleating agents, PP transcrystallization has taken place on the fibre surface [9]. On the other hand, very little has been investigated on the effect of organic textile fibres on PP crystallization [10–13] and the influence of fibre treatment has not been included in those studies due to the non-existence of commercial coupling agents simultaneously reactive with both the organic fibres and polyolefine matrices.

Previous studies carried out in our laboratories to investigate the reinforcing effect of textile fibres on thermoplastic

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Table 1
Crystallization parameters of PP in composites based on short PET and PA fibre-filled PP

	T_c (K)	Plain PP	PP + PET nat	PP + PET mod (1:1)	PP + PET mod (1:2)	PP + PA nat	PP + PA mod
n	398	2.60	1.47	1.41	2.24	2.76	2.42
	403	2.75	2.08	1.31	1.85	2.98	2.80
	405	2.70	2.32	1.48	1.87	3.00	2.73
	408	2.77	1.94	1.74	1.64	2.86	2.86
$\tau_{1/2}$ (s)	398	137.6	68.4	66	28.2	98.4	173.4
	403	479.2	288.8	247.2	93.6	354	742.0
	405	856.1	546.2	421.9	218.4	621	1369.9
	408	2001.6	1319.6	979.2	585.6	1277.4	3031.9
$-\log K_n$ (min)	398	1.09	0.24	0.22	0.57	0.75	1.27
	403	2.64	1.58	0.96	0.52	2.46	3.22
	405	3.27	2.38	1.41	1.21	3.20	3.87
	408	4.38	2.76	2.27	1.78	3.96	5.03

matrices have shown that polyethylene terephthalate (PET) and nylon 66 (PA) fibres increase the stiffness of PP and polyethylene (HDPE, LDPE) matrices [14,15], and the damping, and abrasion and tear strength of elastomers [16]. The influence of PET chemical treatment with a sulfonyl diazide, developed in our laboratories [17], on the mechanical behaviour of the above-mentioned thermoplastic composites was also investigated [18].

In the present study it is intended to analyse the morphology of composites based on PP filled with unmodified and azide-modified PET and PA fibres, and to evaluate the kinetic parameters and thermodynamic characteristics.

2. Experimental

iPP (melt flow index 2.9, at 190°C and 5 kg, and density 0.905 g cm^{-3}), supplied by Repsol Química S.A. under the trade name Isplen PP-051, and short textile PET and PA fibres, supplied by Velutex-Flock, S.A., were used in the present study. In order to improve the adhesion at the fibre/matrix interface, sulfonyl azide groups have been introduced into the chemical structure of the fibres by reaction with *p*-sulfonyl-benzoyl diazide. Both, the product and the process were previously developed in our laboratories [19,20]. The chemical structure of PET fibres presents two hydroxyl final groups capable of reaction with the azide derivative. This reaction was carried out at PET/azide molar ratios of 1/1 and 1/2, so, one or two sulfonyl azide groups, respectively, were present on the PET structure. In the case of the PA fibres, only a PA/azide molar ratio of 1/1 was used.

The compounding was carried out in a roll-mill, at 170°C, and for a period of time of 20 min. Once the polymer was melted, the appropriate percentage of fibre was added (20% by weight). The obtained compounds were compression molded at 200°C in a Collins press. From the molded plaques, samples were taken for the crystallization studies. The temperatures of crystallization that have been used in this study are shown in Tables 1 and 2.

The morphology of the matrix was studied on thin films by using an optical polarizing microscope Leika Metalographic

Table 2
PP crystallization parameters of PET and PA short fibre composites

	T_c (K)	Plain PP	PP + PET nat	PP + PET mod (1:1)	PP + PET mod (1:2)	PP + PA nat	PP + PA mod
$T_m°$		471.1	457.6	458.0	463.1	462.4	474.9
T_m (K)	398	438	437.3	439.8	439.4	439.2	437.1
	403	440	439.6	440.9	440.4	440.4	438.9
	405	331.2	439.5	441.5	441.4	441.1	440.4
	408	442.5	440.8	443.0	443.1	442.9	442.0
$T_m/T_c\Delta T$ ($\times 10^2$)	398	1.51	1.84	1.84	1.70	1.71	1.43
	403	1.61	1.99	1.99	1.82	1.84	1.51
	405	1.65	2.06	2.05	1.87	1.89	1.56
	408	1.72	2.17	2.17	1.97	1.99	1.62
$1/n\ (\log K_n) + \Delta F/2.3RTc$	398	2.55	2.81	2.82	3.23	2.70	2.45
	403	1.89	2.09	2.12	2.57	2.03	1.70
	405	1.59	1.78	1.85	2.16	1.73	1.38
	408	1.16	1.32	1.44	1.66	1.36	0.98
σ_e (erg/cm^2)		185.9	127.4	118.6	152.8	136.6	216.7

Aristomet model, with a Mettler FP-90 automatic hot-stage thermal control. Samples were sandwiched between microscope cover glass, melted at 200°C for 10 min and then rapidly cooled to the crystallization temperature. The PP spherulitic growth was observed by taking photomicrographs at due intervals of time.

The crystallization kinetics are described by the Avrami equation [21,22], and several methods can be used to study the PP crystallization, for example by measuring the density, specific volume or heat, electric resistivity, and enthalpy.

In this case, the crystallization kinetics and thermal properties of the matrices have been determined in a DSC-7 Perkin-Elmer differential scanning calorimeter coupled with a data station PE 7700, with the following standard procedure: the samples (about 10 mg) were melted at 200°C for 10 min in order to eliminate any thermal history of the material, then were cooled to the crystallization temperature, T_c, and maintained at that temperature for the necessary time for the complete crystallization of the matrix. The heat evolved during the isothermal crystallization (ΔH_c) was recorded as a function of time, at different crystallization temperatures. The experiments were carried out in nitrogen atmosphere and the scans were obtained at 10 K/min. The isotherms were constructed by integrating the area under the exothermic peak. In all calculations a crystal heat of fusion of 209 g^{-1} has been taken for the polypropylene [23].

After crystallization the samples were heated to the melting point at a rate of 10 K min^{-1}. The melting temperatures (T_m) of the composites were obtained from the maximum of the endothermic peaks. The equilibrium melting temperatures (T_m^0) were obtained from the melting temperature versus crystallization temperature plots (Hoffman–Weeks plots).

The kinetic parameters of the polymers, such as the crystallization kinetic constant (K_n) and the Avrami exponent (n), have been calculated from the Avrami equation [21,22]. These parameters can be used to interpret qualitatively the nucleation mechanism and morphology, and overall crystallization rate of the polymers, respectively.

Finally, the crystallization thermodynamic and kinetic of the samples have been analysed on the basis of the secondary nucleation theory of Hoffman and Lauritzen [24] that is expressed by the next equation:

$$(1/n)\log K_n + \Delta F/2.3RT_c = A_0 - (4b_0\sigma\sigma_e T_m)/(2.3k_B\Delta H_f T_c\Delta T) \quad (1)$$

where $\Delta T = T_m^0 - T_c$, σ and σ_e are the free energies per unit area of the surfaces of the lamellae parallel and perpendicular to the chain direction, respectively. ΔH_f is the enthalpy of fusion and b_0 is the distance between two adjacent fold planes. If it is assumed that the spherulite nucleus density is independent of time, ΔT, blend composition and T_m, then A_0 may be considered constant. ΔF is the activation energy for the transport process at the liquid–solid interphase and can be calculated with a high precision from the Williams–Landel–Ferry equation [25], given by the next expression:

$$\Delta F = F_{WLF} = (C_1T_c)/(C_2 + T_c - T_g) \quad (2)$$

where C_1 and C_2 are constants whose values are assumed to be 4.12 kcal mol^{-1} (17.24 kJ mol^{-1}) and 51.6 K, respectively (the T_g of pure PP was taken as 260 K). When plotting ($1/n$) log $K_n + \Delta F/2.3RT_c$ *versus* $T_m{\cdot}T_c\Delta T$, the value of $4b_0\sigma\sigma_e/k_B\Delta H_f$ can be calculated from the slope of the straight lines, and having in mind that b_0, σ, ΔH_f, and the Boltzann constant, k_B, have the following values given by the literature: 5.24 Å, 11 kJ m^{-2}, 209 J g^{-1}, and 1.35×10^{-16} erg/mol K, respectively, it is possible to calculate the value of the free energy of folding of isotactic polypropylene lamellar crystals, σ_e, as a function of composite composition.

3. Results and discussion

The effect of the fibres and their chemical treatment on the matrix crystallization can be analysed from Fig. 1, where the crystallization isotherms of the PP composites with unmodified and azide-modified PET (A) and PA (B) fibres, at 403 K, are graphically represented. It can be deduced that the PP crystallization rate increases in the presence of PET fibres, and this increase is more sensible with the azide-modified PET fibres which suggests that the nucleant effect of the fibre increases with its chemical treatment. At the same crystallization temperature, the higher the modification degree of the PET fibre, the faster the PP crystallization. So, independently of the crystallization temperature (T_c), the half time of PP crystallization ($\tau_{1/2}$) decreases in the presence of PET fibres and with the azide content, as can be seen in Table 1. However, in the case of the PA fibres, if it is of course true that the unmodified PA fibres act as nucleating agents, as confirmed by the decrease of $\tau_{1/2}$ values, the azide-modified fibres delay the PP crytallization, as shown in Table 1.

From the above results it is deduced that PET fibre is an effective nucleating agent for PP, and this effect increases in the presence of sulfonyl azide groups. Generally speaking, the decrease of $\tau_{1/2}$ is independent of the crystallization temperature. Unmodified PA fibres also act as a nucleant for PP although, in this case, the effect of the modification with the azide compound is opposite to that observed with modified PET fibres.

The PP spherulitic growth rate, in the presence of fibres and at different temperatures, was investigated and the results are graphically represented in Fig. 2. It has been shown that the PP spherulitic growth rate is not influenced by the fibre and its chemical treatment, and only depends on the crystallization temperature. In all cases, the PP spherulitic growth rate, expressed as the increase of the spherulite

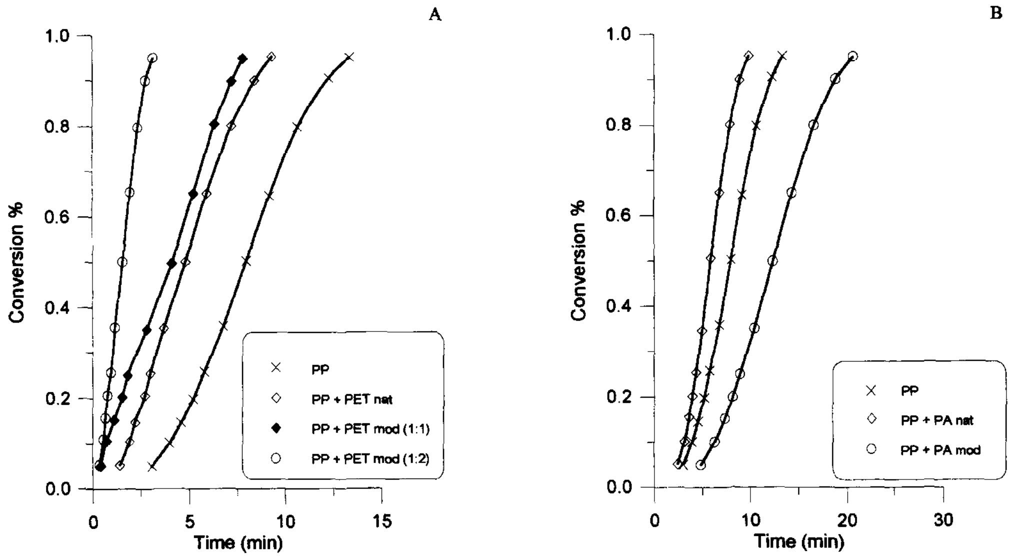

Fig. 1. Crystallization isotherms of PP with unmodified (NAT) and azide-modified (MOD) polyethylene terephthalate (PET) and nylon 66 (PA) short fibres, at 403 K.

radius versus time, at 398, 403 and 405°C, were 0.09, 0.13 and 0.38 μm s^{-1}, respectively.

The presence of PP transcrystallinity on the fibre surface as a function of fibre type and crystallization temperature has also been investigated, and, as can be deduced from the microphotographs of Fig. 3, untreated PET fibres gives rise to PP transcrystallization independently of the crystallization temperature. However, the PP does not crystallize on the surface of the azide-modified fibres although at very high undercooling temperature (298 K) it looks like this phenomenon is appearing. So, it can be concluded that the azide treatment of the fibres obstructs the PP transcrystallization and that this phenomenon is favoured at high undercoolings or low crystallization temperatures. As will be shown in a future paper, the adhesion at the fibre/PP interface improves with the azide treatment of the fibres which in turn gives rise to an increase in the composite stiffness. These results are not in opposition to the theory that transcrystallinity can be responsible for an increase in the mechanical properties of composites, but in the opposite, show that a good adhesion at the interface and transcrystallinity do not have to simultaneously take place.

In the case of the PA fibres, unmodified fibres show a very noticeable transcrystalline growth of PP on their surface that is not so noticeable in the azide-modified PA fibres, at least at low undercooling temperatures. However, the PP transcrystallinity appears again at higher undercooling temperatures (298 K), as shown in Fig. 4.

By plotting the Avram equation in its logarithmic form, a semi-quantitative analysis of the isothermal crystallization of the matrix versus time has been carried out. From Fig. 5 the Avrami parameters, n, and the kinetic constants, K_n, of the different composites were calculated as compiled in Tables 1 and 2. In all cases, fractionary values of n have been obtained. Statistically, in the Avrami crystallization theory, fractionated values of n are accepted assuming a partial time of overlapping of the primary nucleation and crystal growth [26].

The values of n for the unmodified or azide-modified PET fibre-filled PP composites are near or below two which correspond to a heterogeneous and instantaneous nucleation with a mono- or bidimensional spherulitic growth, while in the case of the unmodified or azide-modified PA fibre-filled PP composites are between two and three which is suggesting that a heterogeneous, instantaneous and athermal nucleation with a diffusion-controlled two- or three- dimensional growing is taking place.

The values of the crystallization kinetic constants (K_n) are

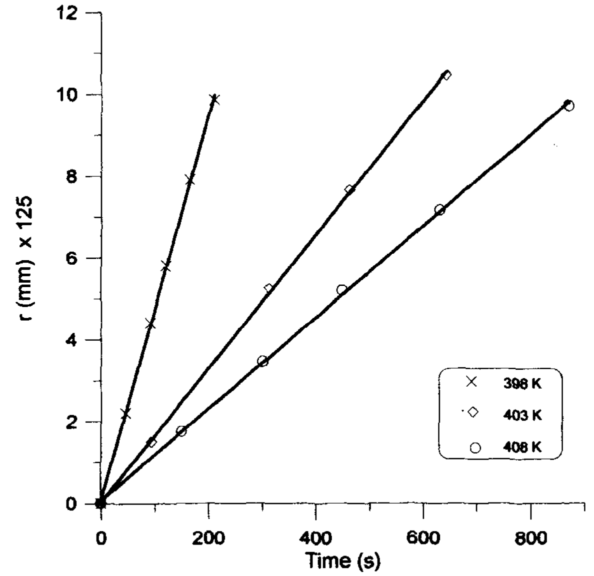

Fig. 2. PP spherulitic growth rate in the plain polymer and in the fibre composites, at different crystallization temperatures.

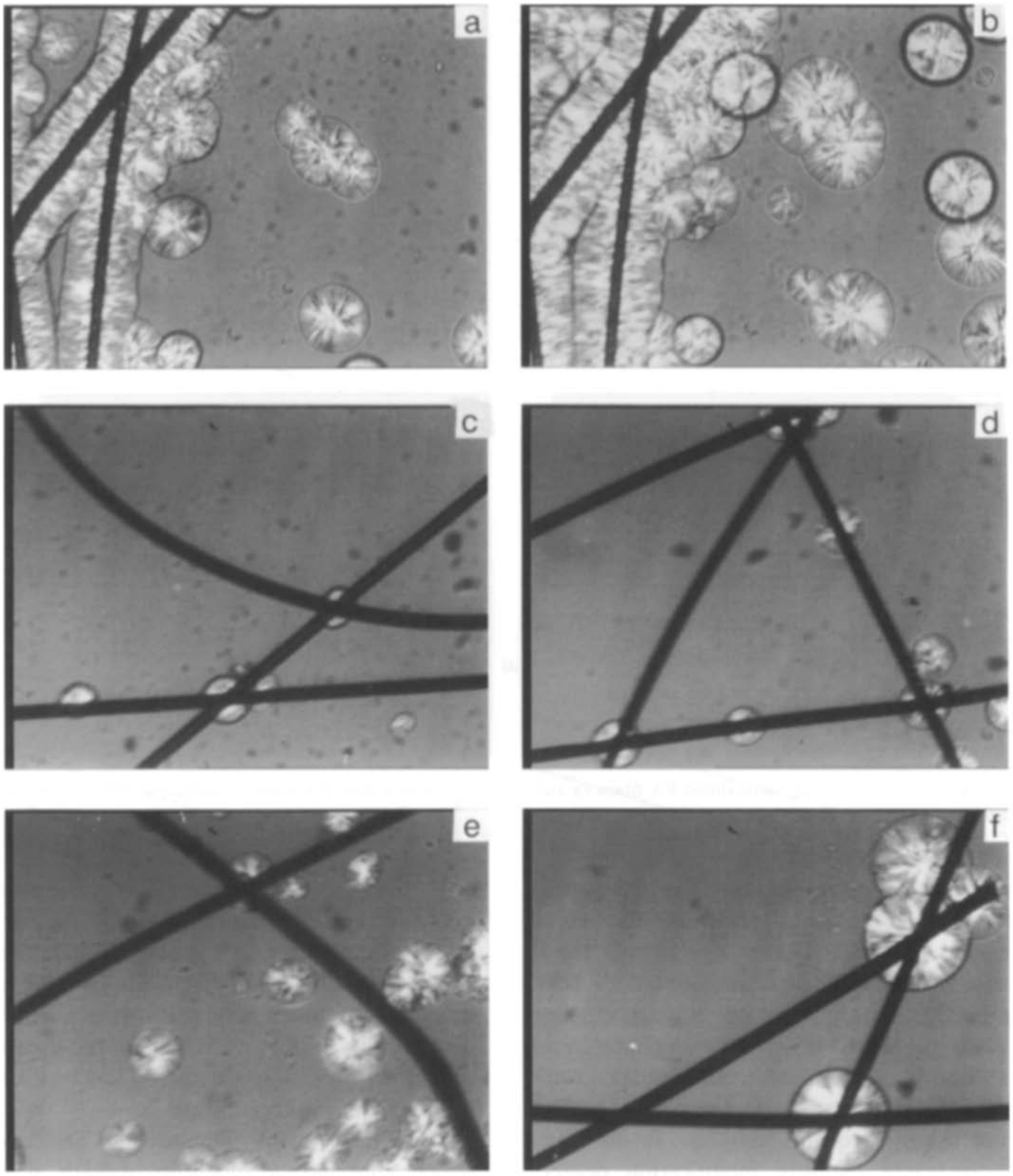

Fig. 3. PP crystallization in the presence of: unmodified PET fibres (a and b), 1/1 azide-modified PET fibres (c and d), and 2/1 azide-modified PET fibres (e and f), at 303 and 298 K, respectively. The microphotographs have been taken at similar intervals of time (125×).

confirming the inferred conclusions from the analysis of the $\tau_{1/2}$ obtained values. That is, for both fibres, the crystallization rate of the polymer matrix decreases as crystallization temperature increases, and unmodified and modified polyester fibres act as nucleating agents for the PP crystallization. In general, at any crystallization temperature, the PP crystallization rate is higher in the presence of PET fibres and increases as the fibre modification degree increases. It can be thought that the better the affinity between the fibres and the polymer matrix the higher the nucleant effect of the fibres and consequently the higher the crystallization rate of the PP. On the other hand, the addition of unmodified PA fibres gives rise to an increase of the PP crystallization kinetic constant, K_n, which indicates the nucleant effect of these fibres on the PP crystallization. However, the azide treatment of the PA fibres delays the PP crystallization as deduced from the increase of $\tau_{1/2}$ as tabulated in Table 1.

The PP melt temperature in the isothermally crystallized samples, determined by d.s.c., from the maximum of the endothermic peaks, are compiled in Table 2. In general, the melt temperature of the polypropylene increases as T_c increases, which is directly related with the polymer crystallite size. However, the melt temperature hardly varies in the presence of PET and PA fibres which is an indication that, at least at this percentage (20%), the fibres hardly affect the spherulitic development of the PP. Previous studies carried out on glass fibre reinforced polypropylene showed that restrictions to the spherulitic development, with a decrease of the PP melt temperature, are observed at fibre contents above 30% in the composite [27].

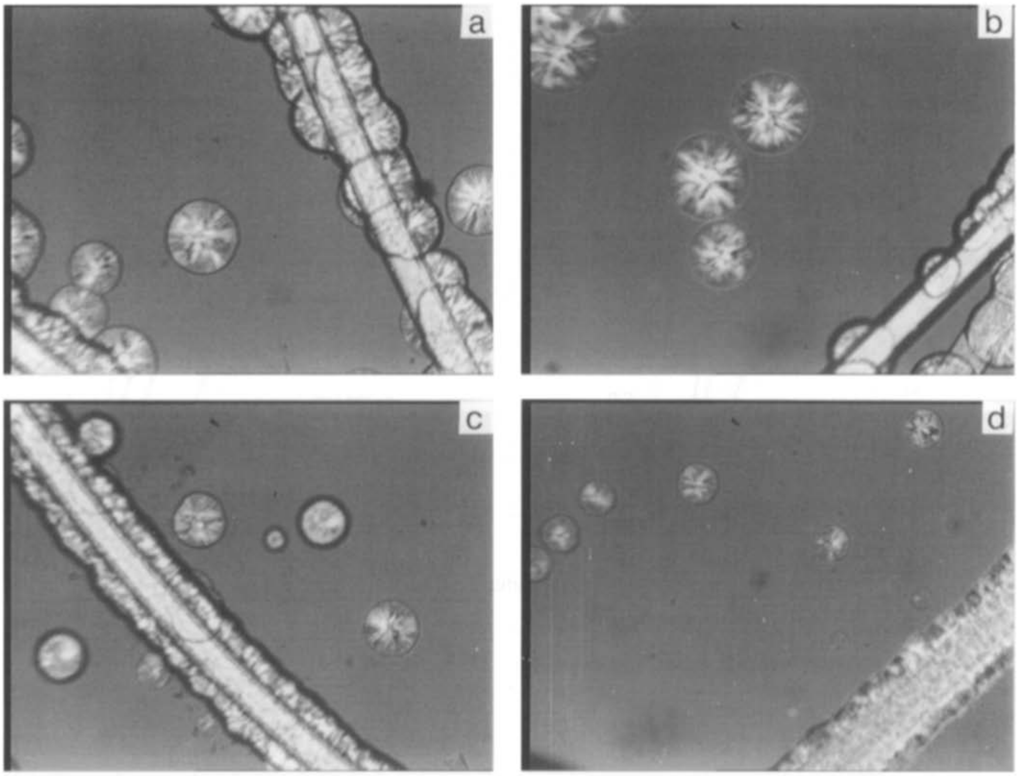

Fig. 4. PP crystallization in the presence of: unmodified PA fibres (a and b), 1/1 azide-modified PA fibres (c and d), at 303 and 298 K, respectively. The microphotographs have been taken at similar intervals of time (125×).

The equilibrium melt temperatures (T_m^0) of PP in the composites were obtained from the Hoffman–Weeks plots (Fig. 6) and compiled in Table 2. The addition of both fibres to the PP gives rise to a decrease of T_m^0 although it tends to increase with fibre modification. These values must be taken into account with some restrictions since two-phase composite materials do not present ideal conditions and comparison of this polymer characteristic in a composite and in the plain polymer is not adequate. However, in the fibre composites, T_m^0 increases as fibre modification degree increases which can be due to an increase of the sample crystallinity.

Finally, the crystallization thermodynamics of the PP, in the melt and in the presence of fibres, were analysed through the secondary nucleation theory of Hoffman–Lauritzen from the plots of Fig. 7. From the obtained values of the interfacial free energy, σ_e, compiled in Table 2, it is observed that σ_e decreases in the presence of fibres although they tend to increase with fibre modification.

4. Conclusions

From the above results the following conclusions can be deduced:

Unmodified and modified PET fibres act as nucleating agents for PP crystallization, giving rise to an increase of the global rate of the crystallization process.

Unmodified PA fibres act as a nucleating agent for PP crystallization. However, in this case, the azide modification of PA fibres gives rise to a delay of PP crystallization.

The unmodified PET fibres and both the unmodified and modified PA fibres give rise to the phenomenon of transcrystallinity with PP, which permits increasing the interaction at the fibre/matrix interface and hence the mechanical properties of the composites.

The PET and PA fibres do not affect to the PP melt temperature and the spherulitic growth, at least in the percentage that has been used in this study (20%).

Unmodified and modified PET fibres give rise to a decrease of the Avrami exponent, n, in the composites, which indicates that a unidirectional crystalline growth is favoured, probably due to the development of transcrystallinity, although in some cases it has been observed only at high undercoolings.

In general, it can be established for the studied composites that the spherulitic development of the polymer matrix comes from an instantaneous and athermic nucleation whose growth is not constant (fractionary values of n).

The energy of PP chain folding decreases in the presence of fibres, although it increases with the degree of fibre modification.

Finally, it must be pointed out that both transcrystallinity and good adhesion at the interface permit increased stiffness of the composites although any or both phenomena make take place independently of each other.

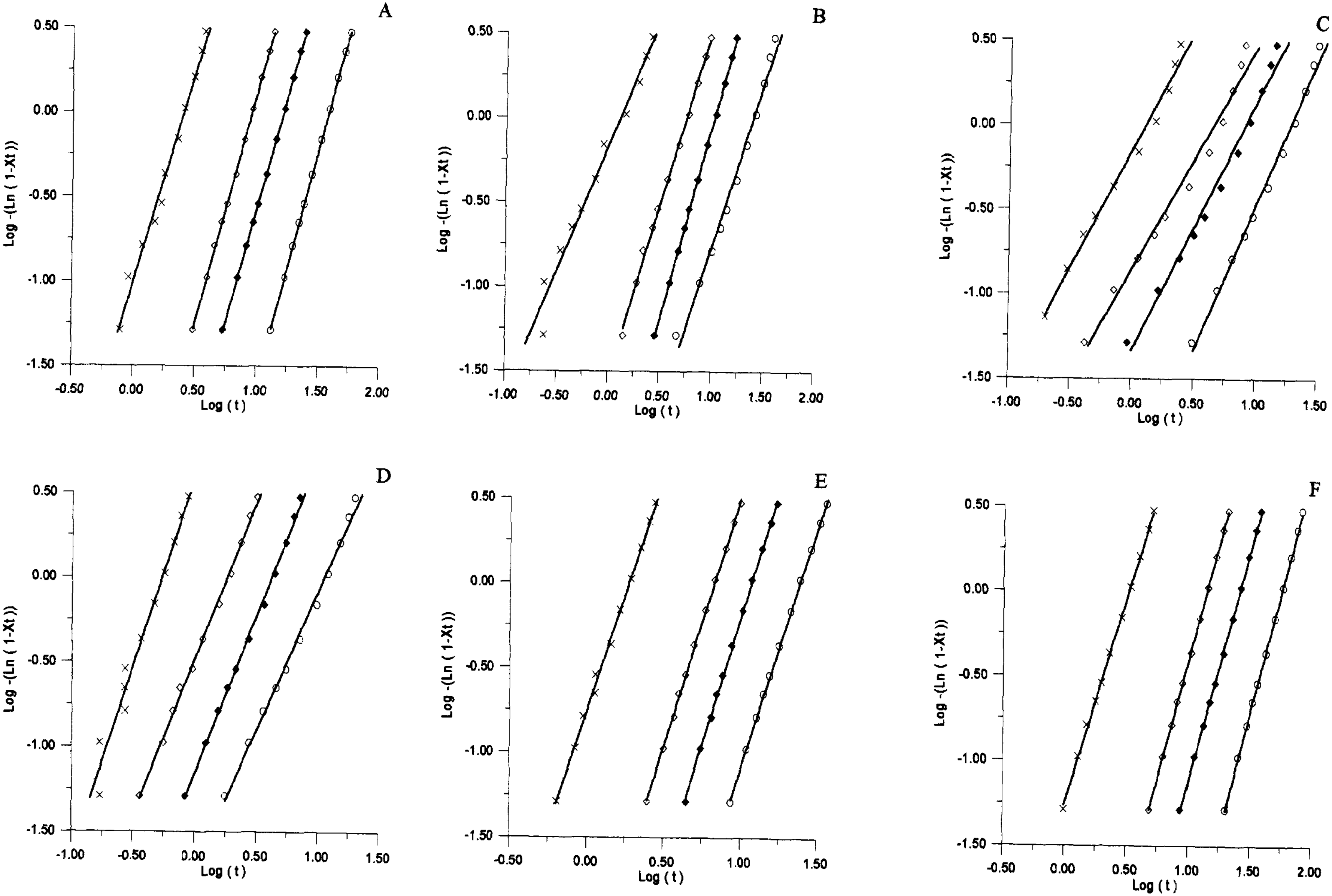

Fig. 5. Avrami plots of PP in the plain polymer (A), and in the presence of unmodified (B), and 1/1 (C) and 1/2 (D) azide-modified PET fibre composites, and unmodified (E) and azide-modified (F) PA fibre composites, at different temperatures: 398 K (x), 403 K (◇), 405 K (◆), and 408 K (○).

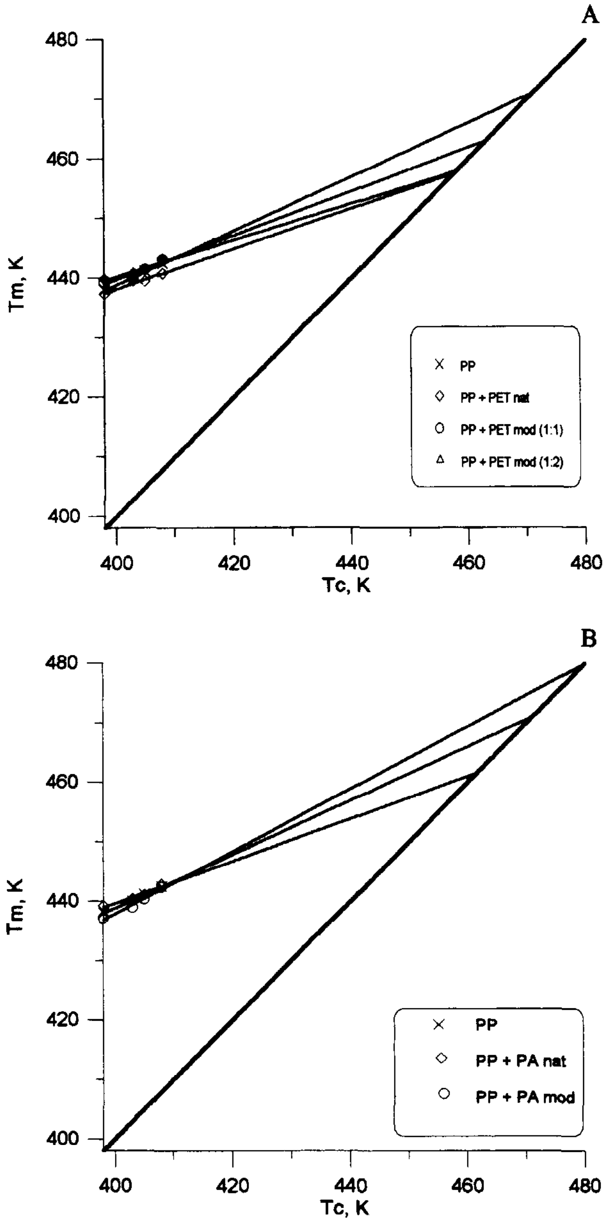

Fig. 6. Hoffmann–Weeks plots of PP in PET (A) and PA (B) fibre composites.

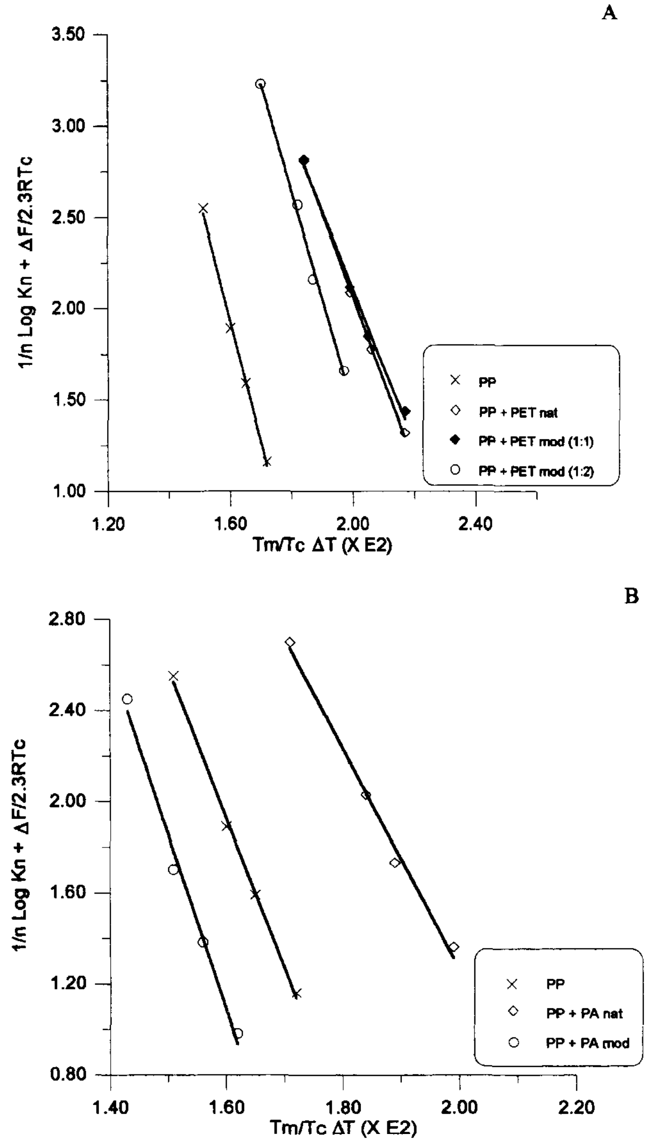

Fig. 7. Calculation of σ_e values for PP in the PET (A) and PA (B) fibre composites.

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